

PREPARATION AND CHARACTERIZATION OF NANOSIZED ULTRAMARINE BLUE PIGMENT FROM NATURAL KAOLIN SAMPLE

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Abstract

The aim of this research is the preparation of nanosized Ultramarine blue pigment for the production of pozzolanic cement. Ultramarine blue pigment was made from natural kaolin which was collected from Kyaukpataung Township, Mandalay Region, Myanmar. pH of natural kaolin sample was determined and then was characterized by EDXRF, XRD, SEM, FT IR and TG-DTA techniques. All of the results showed that natural kaolin sample had appropriate properties for the preparation of nanosized Ultramarine blue pigment. The procedure for the preparation of Ultramarine blue pigment involved the heat activation of kaolin. The activated kaolin was then characterized by XRD and SEM techniques. The comparison of XRD patterns of activated kaolin with natural kaolin sample showed that most peaks of the kaolinite mineral disappeared in activated kaolin. The average crystallite size of activated kaolin was 35.86. The comparison of SEM images of activated kaolin with natural kaolin sample showed that smaller aggregates were closer to one another in activated kaolin. Therefore, the natural kaolin sample was transformed into nano metakaolin state during calcination. The yield percent of the prepared Ultramarine blue pigment was 49.32 %. The Ultramarine blue pigment was characterized by XRD, SEM, and FT IR techniques. From analyzed data, Ultramarine blue pigment has cubic crystal form and has cohesive agglomerated structure.

Keywords; Natural kaolin, activated kaolin, Ultramarine blue pigment, calcination

Introduction

Rocks that are rich in kaolinite are known as kaolin or china clay. Kaolin is also known as white clay. Kaolinite clay is a clay mineral, part of the group of industrial minerals, with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Fadzil *et al.*, 2017). Kaolinite clay occurs in abundance in soils that have formed from the chemical weathering of rocks in hot, moist climates, for example in tropical rain forest areas (Thet Thet Han, 2014). Kaolin clay or white clay is rich in kaolinite mineral and also classified as layered silicate mineral. Due to endothermic process or dihydroxylation process, which involves heat, Kaolin particles can easily transform into other shape or particles (Morsy, 2012). The reaction of endothermic process will create kaolin into metakaolin, nano metakaolin and nano metaclay and slight increment of silica content were produced (Fadzil *et al.*, 2017).

In literature, the chemical composition weight % of natural kaolin are SiO_2 -48.5, Al_2O_3 -38, Fe_2O_3 -1.1, TiO_2 -0.03, CaO -0.10, MgO -0.30, K_2O -1.85, Na_2O -0.10. The silicon and aluminium ratio in china kaolin is 1.13. China kaolin has as minority minerals illite and orthoclase and the activation temperature of kaolin was 700 °C (Sancho *et al.*, 2008). The primary use of kaolin is the paper industry. Kaolin has a variety of other uses in products including paint, rubber, cable insulation, specialty films and fertilizers (Lvorkin, 2012).

The history of Ultramarine blue goes back to Bible times, being still used widely today. The natural material with the typical colour is the mineral lazurite (Sancho *et al.*, 2008). Lazurite or natural Ultramarine is arguably the most expensive source of blue pigment. Natural Ultramarine was undoubtedly the most favoured blue colour: the pigment worked well in water and oil, did not fade, and gave a very consistent shade (Hamerton *et al.*, 2013).

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The applications of Ultramarine are diverse and include the production of plastics, paints and powder coatings, printing inks, paper and paper coating, rubber and thermoplastic elastomers, latex products, detergents, cosmetics and soaps, artists' colours, toys and educational equipment, lather finishes, powder markers, roofing granules, synthetic fibers, theatrical paints and blue mattes, cattle salt licks and white enhancer (Buxbaum and Pfaff, 2005).

Materials and Methods

All chemicals used in this work consist of the product from British Drug House (BDH). Chemicals are stated in each of the experiment. The apparatus used in this paper include a Balance (E Mettler, Switzerland), pH meter (Jenway 4330, Labquip, England), Scanning Electron Microscope (JEOL JSM - 5610 series), Energy Dispersive X-Ray Fluorescence Spectrometer (NEXCG-Rigaku), X-Ray Diffractometer (XRD-Regaku-D-Max-2200, Japan), Thermo Gravimetric Analyzer (Model –Universal V 2.5 H. Hi-Res TGA 2950, TA Instrument, Japan) and Reflection Transmission Color Densitometer (Noritsu DM 1).

Sample Collection and Characterization of Natural Kaolin Sample

Natural kaolin sample was collected from Kyaukpataung Township, Mandalay Region, Myanmar. Qualitative elemental composition of natural kaolin sample was determined by EDXRF technique. Natural kaolin sample was characterized by XRD, SEM, TG-DTA and FT IR techniques at Universities' Research Centre, University of Yangon.

Preparation and Characterization of Activated Kaolin Samples

Natural kaolin sample was pulverized in a ball mill and sieved (240 mesh) to obtain the powdered sample. pH of powder sample was determined. The powder sample was then calcined at 600 °C for two hours and activated kaolin sample was obtained. Activated kaolin sample was characterized by XRD, SEM, TG-DTA and FT IR techniques at Universities' Research Centre, University of Yangon.

Preparation and Characterization of Ultramarine Blue Pigment

A mixture of 3.0 g of activated kaolin sample, 3.2 g of anhydrous sodium carbonate, 3.0 g of sulphur, 0.4 g of silica and 0.4 g of charcoal were pulverized in a mortar and pestle. It was placed in a crucible with lid and sealed tight using wet fire clay. Crucible with mixture was calcined at 700 °C, 750 °C, 800 °C, 850 °C and 900 °C for three and half hours, Ultramarine blue pigment was obtained. It was stored in a desiccator for further characterization.

The solubility of Ultramarine blue pigment was tested with various solvents and colour density was also determined. Ultramarine Blue pigment was characterized by XRD, SEM, TG-DTA and FT IR techniques at Universities' Research Centre, University of Yangon.

Results and Discussion

The photograph of natural Kyaukpataung kaolin sample is shown in Figure 1. pH value of natural kaolin sample is presented in Table 1.



Figure 1 The photograph of natural kaolin sample

Table 1 pH Value of Natural Kaolin Sample

Sample	pH	*Literature pH
Natural kaolin	4.05	4-5

*Keller, 1990

Characterization of Natural Kaolin Sample

EDXRF analysis

The mineral oxide composition of collected natural kaolin sample is presented in Table 2. Natural kaolin is rich in aluminium oxide and silicon dioxide. Theoretical ratio of Si: Al in pure kaolin is 1.04 (Lvorkin, 2012). The ratio of Si: Al in collected natural kaolin sample was found to be 1.67. The collected natural kaolin sample has a bit less alumina and more silica. It was not detected the oxide of magnesium, manganese and sodium as reported by Sancho *et al.* (2008).. Moreover, it was found to have less potassium, iron, titanium and calcium.

Table 2 EDXRF Analysis for Natural Kaolin Sample

Metal Oxide	Mass (%)	Reported value*(%)
MgO	-	0.30
Al ₂ O ₃	33.800	38.00
SiO ₂	64.100	48.50
P ₂ O ₅	0.134	-
K ₂ O	0.054	1.85
CaO	0.041	0.10
TiO ₂	0.453	0.03
Fe ₂ O ₃	0.682	1.10
Na ₂ O	-	0.10
MnO	-	-

*Sancho *et al.*, 2008

XRD analysis

The X-ray diffractogram of natural kaolin sample is presented in Figure 2. According to XRD analysis, the diffraction pattern was well-matched with kaolinite Al₄(OH)₈(Si₄O₁₀), aluminium silicate hydroxide. From X-ray diffractogram of natural kaolin sample, the average crystallite size can be calculated. According to Debye Scherrer Equation, the average crystallite size of natural kaolin sample was found to be 27.95 nm.

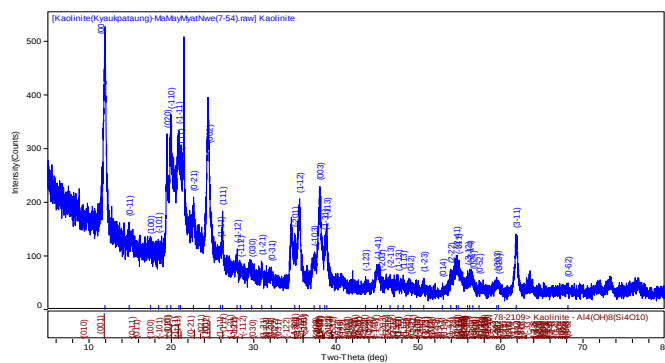


Figure 2 X-ray diffractogram of natural kaolin sample

SEM analysis

The SEM image of natural kaolin sample is presented in Figure 3. In SEM micrograph of sample, shape and surface texture can be seen. From literature, the shape of kaolin is flaky and platy form and whitish layer represent by alumina system (Fadzil *et al.*, 2017). From the SEM micrograph of natural kaolin sample it was in layer or flakes with spherical particles.

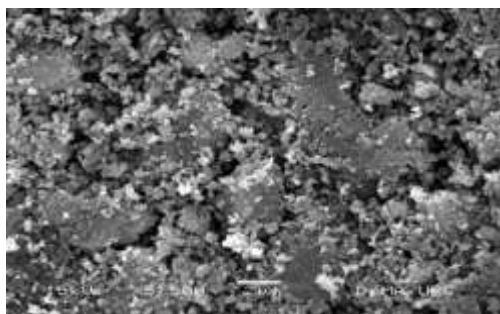


Figure 3 SEM image of natural kaolin sample

FT IR spectrum and band assignments

FT IR spectrum of the studied sample is presented in Figure 4. Kaolinite has absorption bands between 3500 cm^{-1} and 3750 cm^{-1} correspond to stretching frequencies of OH groups (Wilson, 2003) where three characteristic bands (3693 cm^{-1} , 3653 cm^{-1} and 3619 cm^{-1}) are defined. If the band at 3670 cm^{-1} disappears, Kaolinite structure is disordered and easier to dehydrate (Bich *et al.*, 2009). But kaolinite present in the analyzed sample has an ordered structure, since the three bands are defined (Vaculíková *et al.*, 2011). The FT IR spectrum of natural kaolin sample showed band at 3693 cm^{-1} , 3653 cm^{-1} and 3619 cm^{-1} indicate partial ordered structure of this sample Figure 4. Diffused bands observed at about 3473 cm^{-1} and 1631 cm^{-1} , which are attributed to the stretching and deformation vibrations of the physically adsorbed water (O-H) molecules at the surface, respectively. The most pronounced OH stretching bands in Kaolinite are the inter hydroxyl bands 3620 cm^{-1} , and the most intense band is located at 3693 cm^{-1} (Fernandez, 2005). The next three bands in the spectrum of kaolinite (1114 cm^{-1} , 1031 cm^{-1} and 1008 cm^{-1}) also have a consensual assignment by the different literature sources (Fernandez, 2005). These are the most intense Si-O stretching modes, and can be observed in most of the silicate minerals. According to the literature, two bands at 777 cm^{-1} and 713 cm^{-1} could be attributed to asymmetric stretching in Si-O-Al bonds (Fernandez, 2005). And then, low intensity peaks at about 530 cm^{-1} and 450 cm^{-1} appeared; the bands at 792 cm^{-1} , 752 cm^{-1} , 694 cm^{-1} , 534 cm^{-1} , 466 cm^{-1} and 430 cm^{-1} were assigned to quartz. The observed quartz peaks were weak in this FT IR spectrum. Selective kaolin has very similar with the literature value of kaolinite sample.

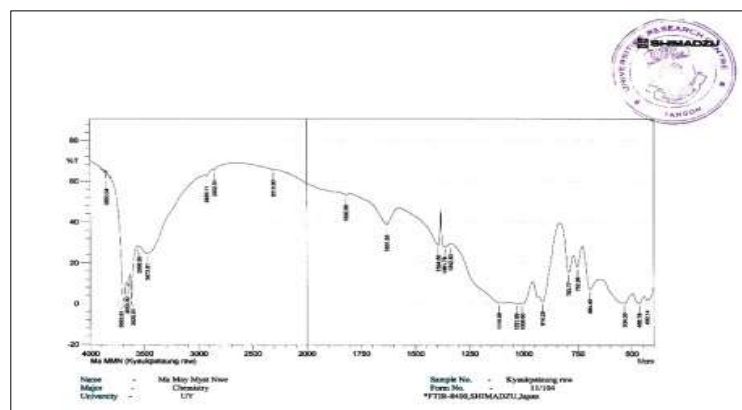


Figure 4 FT IR spectrum of natural kaolin sample

Thermal analysis for natural kaolin sample

TG-DTA thermogram of natural kaolin sample is presented in Figure 5. Thermogram was found to have two endothermic peaks at 63.18 °C and 574.4 °C. First peak was observed due to the dehydration of natural sample and second endothermic peak was attributed to the decomposition of organic compounds and removal of structural water (Vahideh, 2014). Because of high decomposition temperature for organic compounds and structural water, they were tightly bound in systematic arrangement of natural kaolin sample. The small amount of reliable weight loss was observed 12.89 % in the TGA. Thus, the natural kaolin sample contains low impurities and organic compounds. Therefore, the calcination temperature for the natural kaolin sample was chosen as 600 °C for activation.

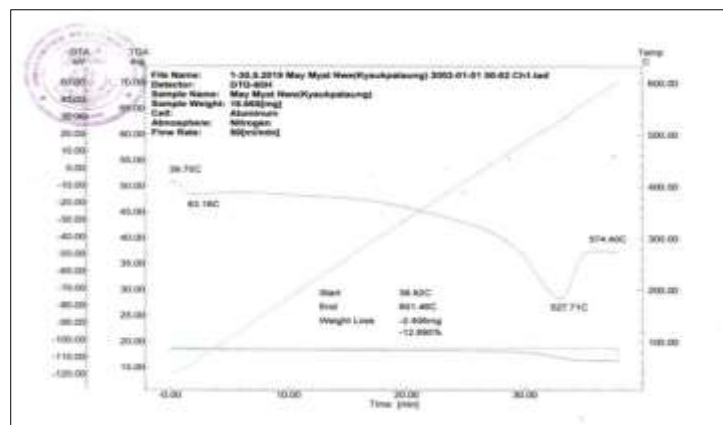


Figure 5 TG-DTA thermogram of natural kaolin sample

Characterization of Activated Kaolin Sample

X-ray diffractogram of activated kaolin sample obtained by calcination of natural kaolin at 600 °C for 2 h is presented in Figure 6. The comparison of XRD pattern of activated kaolin with natural kaolin sample revealed that most peaks of the kaolinite mineral disappeared at the 600 °C. Therefore, dehydroxylation and transformation of kaolinite into metakaolin have been performed completely as described by Moodie et al. (2011). The average crystallite size of activated kaolin after calcination was calculated. According to Debye Scherrer Equation, the average crystallite size of activated kaolin was 35.86 nm. The average crystallite size of activated kaolin was larger than natural kaolin and it was assumed to be accumulated nature of particles.

The SEM image of activated kaolin sample is presented in Figure 7. The comparison of SEM images of activated kaolin with natural kaolin sample showed that flakes with spherical form as well as agglomerates, smooth surface and uniform texture were observed in the former. Smaller aggregates were closer to one another, similar to nano metakaolin. That is, shape and surface texture were similar to metakaolin. The flakes form was similar to nano metakaolin (Fadzil *et al.*, 2017). Therefore, meta or nano metakaolin may be formed after calcination.

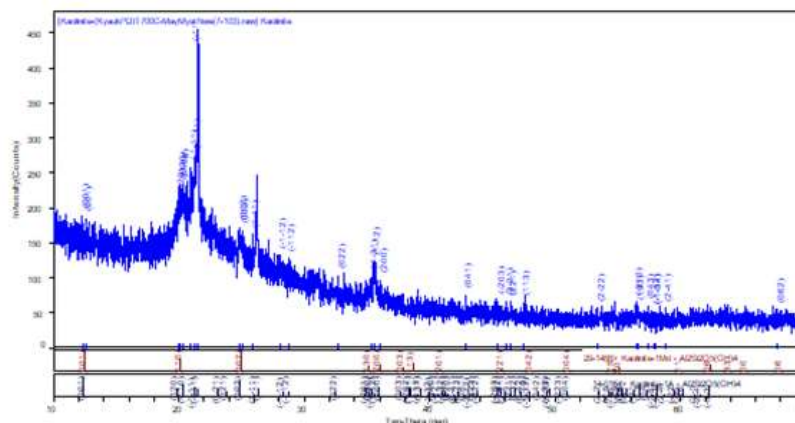


Figure 6 X-ray diffractogram of activated kaolin sample

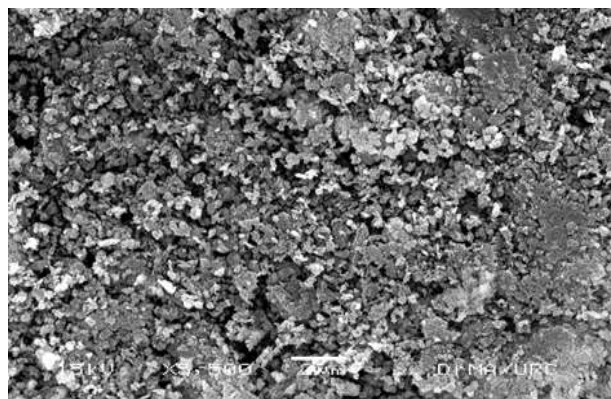


Figure 7 SEM image of activated kaolin sample

Colour Density and Solubility Test of Ultramarine Blue Pigment

The photograph of Ultramarine blue pigment prepared using natural kaolin sample (850 °C and 3:30 h) is shown in Figure 8. The yield percent of the prepared Ultramarine blue pigment from Natural kaolin sample was observed as 49.32%.



Figure 8 The photograph of the prepared Ultramarine blue pigment

Colour density

The colour observation obtained in final calcination step are presented in Table 3. It was observed that the colour observations vary with different calcination temperatures. In this table, it was found that 850 °C temperature gave mature navy blue colour for Ultramarine blue pigment. Colour density of Ultramarine blue pigment was observed as 1.14D.

Table 3 Colour Observation of Prepared Pigment Using Different Temperatures

No.	Temperature(°C)	Colour	Remark
1	700	Light coca brown	
2	750	Rosy brown	
3	800	Slate blue	
4	850	Navy blue	Optimum colour
5	900	Burned blue	

Solubility tests

Solubility of Ultramarine blue pigment in different solvents is presented in Table 4. Ultramarine blue pigment was soluble in inorganic acids, moderately soluble in sodium hydroxide and water, and insoluble in organic solvents. Ultramarine blue pigment is polar inorganic compound due to the metal and oxygen linkage (Sancho, 2008).

Table 4 Solubility of Ultramarine Blue Pigment in Different Solvents

No.	Solvents	Results
1	Nitric acid	+
2	Sulphuric acid	+
3	Hydrochloric acid	+
4	Sodium hydroxide (0.1 M)	±
5	Sodium hydroxide (0.01 M)	±
6	Petroleum ether	-
7	Chloroform	-
8	Ethanol	-
9	Ethyl acetate	-
10	Water	±

(+) = soluble (-) = insoluble (±) = moderately soluble

Characterization of Ultramarine Blue pigment

X-ray diffractogram of Ultramarine blue pigment is presented in Figure 9 and Table 5.

XRD results showed the cubic crystal form with axial length 9.2866 Å and the average crystallite size of Ultramarine blue pigment was 36.1 nm. The SEM image of Ultramarine blue pigment is presented in Figure 10. SEM micrograph of Ultramarine blue pigment showed cohesive agglomerated nature, larger and loose cluster. FT IR spectrum of Ultramarine blue pigment is presented in Figure 11. The FT IR band assignments of Ultramarine blue pigment, stretching and bending vibrations of aluminosilicate (Al_2SiO_5) and stretching vibration of S^{3-} ion were observed.

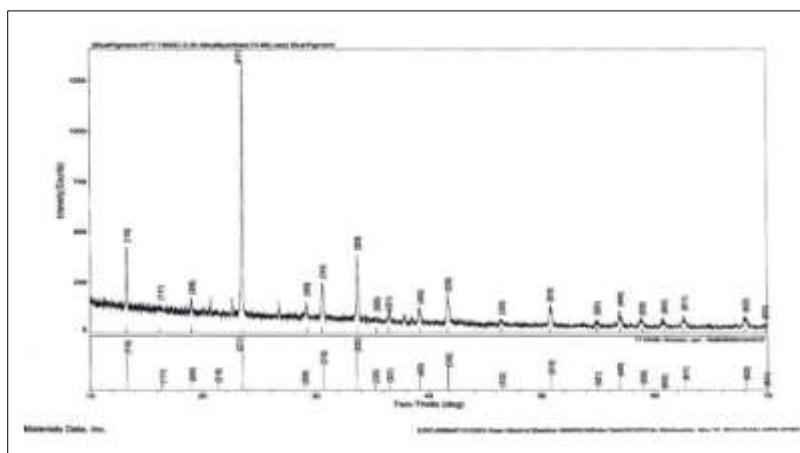


Figure 9 X-ray diffractogram of Ultramarine blue pigment

Table 5 Some Parameters of Ultramarine Blue Pigments Using XRD Analysis

Parameters	Results
Crystal form	Cubic
Lattice constant (Å)	9.2866
Average crystallite size (nm)	36.1

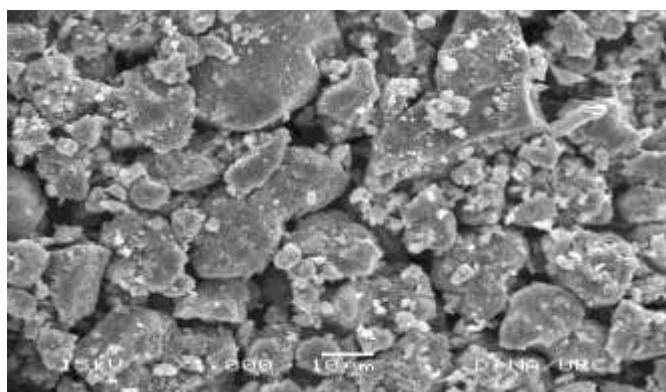


Figure 10 SEM image of Ultramarine blue pigment

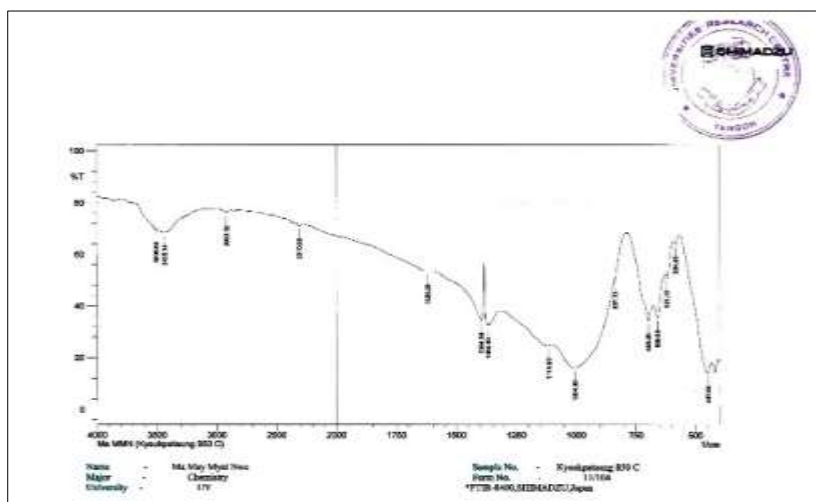


Figure 11 FT IR spectrum of Ultramarine blue pigment

Table 6 FT IR Band Assignment of Ultramarine Blue Pigment

Experimental Frequency (cm ⁻¹)	Literature Frequency* (cm ⁻¹)	Band Assignment
3508	3750-3500	stretching vibration of OH group
3405		
1394	1500-1000	stretching vibration of aluminosilicate (Al ₂ SiO ₅)
1396		
698	950-650	bending vibration of OH group
659		
584	582-547	stretching vibration of S ⁻³ ion
447	550-400	bending vibration of Si-O-Si or Si-O-Al

*Sancho *et al.*, 2008; Vahideh, 2014

Conclusion

This paper revealed that Ultramarine blue pigment can be prepared by using activated kaolin from natural kaolin sample. According to EDXRF analysis, mineral oxide composition of natural kaolin sample is kaolinite. The ratio of silicon and aluminium is 1.67, higher than theoretical ratio (1.04). From the study of characterization of natural and activated kaolin, it can be proved that the qualified kaolin sample is available as natural abundance in Myanmar. Therefore, the natural kaolin sample from Kyaukpataung Township, Mandalay Region, Myanmar, has appropriate properties for the preparation of Ultramarine blue pigment. From analyzed data, the prepared Ultramarine blue pigment has cubic crystal form and has cohesive agglomerated structure.

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